

CLAIMS

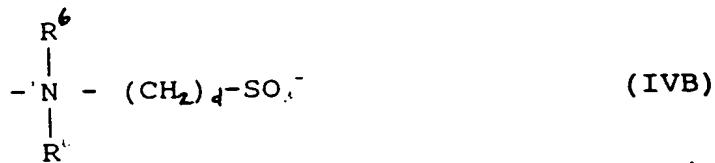
1. A process in which a substrate having a surface which bears substrate pendant functional groups is coated with a coating composition containing a polymer formed from a radical polymerisable monomers including a radical polymerisable zwitterionic monomer and a radical polymerisable monomer containing a reactive group to form a polymer having zwitterionic groups and pendant reactive groups and the said pendant reactive groups are reacted to form covalent bonds with said substrate pendant functional group and thereby form a stable coating of polymer on the said surface, and wherein

said zwitterionic monomer has the general formula I



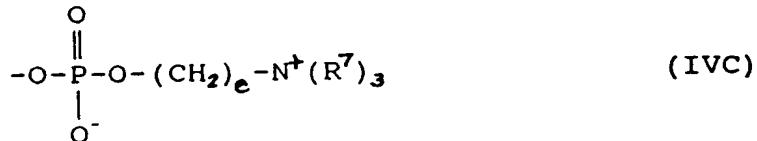
15 wherein B is a straight or branched alkylene, oxaalkylene or oligo-oxaalkylene chain optionally containing one or more fluorine atoms up to and including perfluorinated chains, or if X contains a carbon-carbon chain between B and the centre of permanent position charge or if Y contains a terminal carbon atom bonded to B, a valence bond;

X is a zwitterionic group selected from groups IVB, IVC, IVD, IVE and IVF in which group IVB has the formula



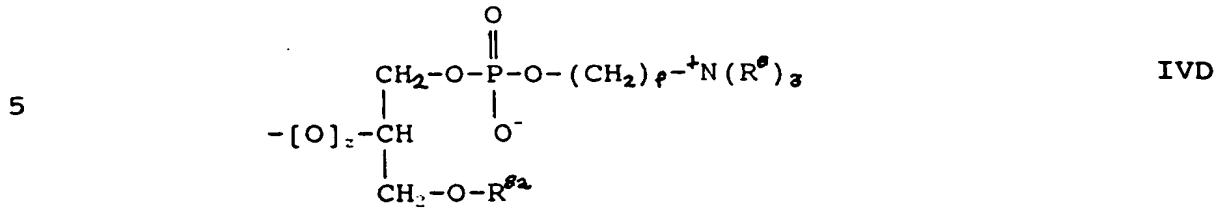
25 wherein the groups  $R^6$  are the same or different and each is hydrogen or  $C_{1-4}$  alkyl and d is from 2 to 4;

group IVC has the formula



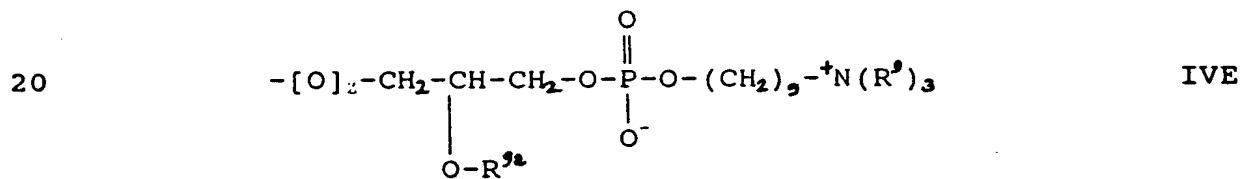
35 where the groups  $R^7$  are the same or different and each is hydrogen or  $C_{1-4}$  alkyl, and e is from 1 to 4;

group IVD has the formula



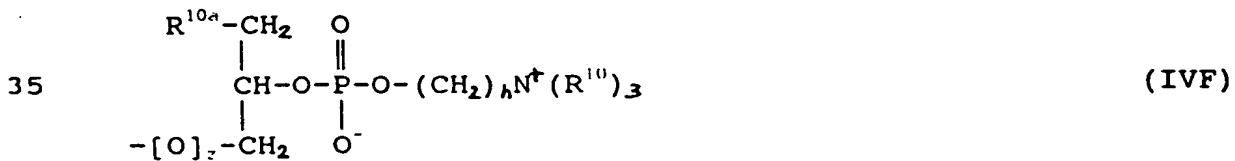
wherein the groups R' are the same or different and each is  
 10 hydrogen or C<sub>1-4</sub> alkyl, R<sup>g<sub>2</sub></sup> is hydrogen or a group -C(O)B<sup>1</sup>R<sup>g<sub>3</sub></sup>  
 wherein R<sup>g<sub>3</sub></sup> is hydrogen or methyl, B<sup>1</sup> is a valence bond or  
 straight or branched alkylene, oxaalkylene or oligo-  
 oxaalkyne group, and f is from 1 to 4; and if B is other  
 15 than a valence bond z is 1 and if B is a valence bond z is  
 0, if X is directly bonded to an oxygen or nitrogen atom  
 and otherwise z is 1;

group IVE has the formula



wherein the groups R' are the same or different and each is  
 25 hydrogen or C<sub>1-C<sub>4</sub></sub> alkyl, R<sup>g<sub>2</sub></sup> is hydrogen or a group -  
 C(O)B<sup>2</sup>R<sup>g<sub>3</sub></sup>, wherein R<sup>g<sub>3</sub></sup> is hydrogen or methyl, B<sup>2</sup> is a valence  
 bond or a straight or branched alkylene, oxaalkylene or  
 oligo-oxaalkylene group, and g is from 1 to 4; and  
 if B is other than a valence bond z is 1 and if B is  
 30 a valence bond z is 0 if X is directly bonded to an oxygen  
 or nitrogen atom and otherwise z is 1; and

group IVF has the formula



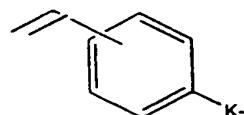
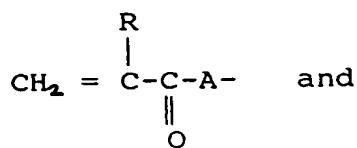
wherein the groups R<sup>10</sup> are the same or different and each  
 is hydrogen or C<sub>1-4</sub> alkyl, R<sup>10a</sup> is hydrogen or a group  
 40 -C(O)B<sup>3</sup>R<sup>10b</sup> wherein R<sup>10b</sup> is hydrogen or methyl, B<sup>3</sup> is a valence  
 bond or a straight or branched alkylene, oxaalkylene or  
 oligo-oxaalkylene group, and h is from 1 to 4; and

if B is other than a valence bond z is 1 and if B is a valence bond z is 0 if X is directly bonded to the oxygen or nitrogen and otherwise z is 1; and

Y is an ethylenically unsaturated polymerisable group

5 selected from

10



wherein:

R is hydrogen or a C<sub>1</sub>-C<sub>4</sub> alkyl group;

A is -O- or -NR<sup>1</sup>- where R<sup>1</sup> is hydrogen or a C<sub>1</sub>-C<sub>4</sub> alkyl group or R<sup>1</sup> is -B-X where B and X are as defined above; and

15 K is a group -(CH<sub>2</sub>)<sub>p</sub>OC(O)-, -(CH<sub>2</sub>)<sub>p</sub>C(O)O-, -(CH<sub>2</sub>)<sub>p</sub>OC(O)O-, -(CH<sub>2</sub>)<sub>p</sub>NR<sup>2</sup>-, -(CH<sub>2</sub>)<sub>p</sub>NR<sup>2</sup>C(O)-, -CH<sub>2</sub>)<sub>p</sub>C(O)NR<sup>2</sup>-, -(CH<sub>2</sub>)<sub>p</sub>NR<sup>2</sup>C(O)O-, -(CH<sub>2</sub>)<sub>p</sub>OC(O)NR<sup>2</sup>-, -(CH<sub>2</sub>)<sub>p</sub>NR<sup>2</sup>C(O)NR<sup>2</sup>-, (in which the groups R<sup>2</sup> are the same or different) -(CH<sub>2</sub>)<sub>p</sub>O-, -  
20 (CH<sub>2</sub>)<sub>p</sub>SO<sub>3</sub>-, or, optionally in combination with B, a valence bond and p is from 1 to 12 and R<sup>2</sup> is hydrogen or a C<sub>1</sub>-C<sub>4</sub> alkyl group, and

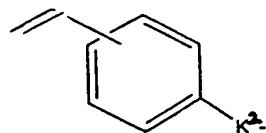
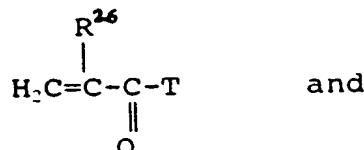
said radical polymerisable monomer containing reactive groups has the formula general formula (XII)

25



where Y<sup>2</sup> is an ethylenically unsaturated polymerisable group selected from

30



where R<sup>26</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl;

35 T is -O- or NR<sup>27</sup>-, wherein R<sup>27</sup> is hydrogen or a C<sub>1</sub>-C<sub>4</sub> alkyl group or R<sup>27</sup> is a group -B<sup>7</sup>Q<sup>3</sup>;

B<sup>7</sup> is a valence bond a straight or branched alkylene oxaalkylene or oligo-oxaalkylene group;

K<sup>2</sup> is a group -(CH<sub>2</sub>)<sub>q</sub>OC(O)-, -(CH<sub>2</sub>)<sub>q</sub>C(O)O-, -(CH<sub>2</sub>)<sub>q</sub>OC(O)O-, -(CH<sub>2</sub>)<sub>q</sub>NR<sup>28</sup>-, -(CH<sub>2</sub>)<sub>q</sub>NR<sup>28</sup>C(O)-,

40

$-(CH_2)_nC(O)NR^{20}-$ ,  $-(CH_2)_qNR^{20}C(O)O-$ ,  $-(CH_2)_qOC(O)NR^{20}-$ ,  
 $-(CH_2)_qNR^{20}C(O)NR^{20}-$  (in which the groups  $R^{20}$  are the same or different),  $-(CH_2)_qO-$ , or  $-(CH_2)_qSO_3-$ , or a valence bond and q is from 1 to 12 and  $R^{20}$  is hydrogen or a  $C_1-C_4$  alkyl group; and

5         $Q^3$  is a reactive group selected from the group consisting of aldehyde groups; silane and siloxane groups containing one or more substituents selected from halogen atoms and  $C_{1-4}$ -alkoxy groups; hydroxyl; amino; carboxyl; 10 epoxy;  $-CHOHCH_2Hal$  (in which Hal is selected from chlorine, bromine and iodine atoms); succinimido; tosylate; triflate; imidazole carbonyl amino; optionally substituted triazine groups; aceloxyl; mesylate; carbonyl di(cyclo)alkyl carbodiimidoyl; and oximino.

15      2. A process according to claim 1 in which  $Q^3$  is selected from the group consisting of aldehyde, reactive silane and siloxane amino, epoxy,  $CHOHCH_2Hal$  (in which Hal is halogen), succinimido, tosylate, triflate, imidazolecarbonyl amino and optionally substituted triazine groups.

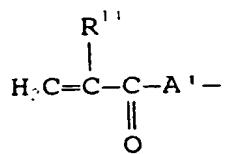
20      3. A process according to claim 1 in which the surface pendant groups are selected from the group consisting of hydroxyl, carboxyl and amine groups.

25      4. A process according to claim 1 in which the polymer is formed from 2-(methacryloyloxyethyl)-2'-(trimethylammonium) ethyl phosphate inner salt and 2-aminoethylmethacrylate and in which the covalent bonding of the pendant amino group is to a surface having pendant carboxylate groups is achieved through the formation of an amide linkage.

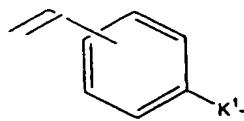
30      5. A process according to claim 1 in which the said radical polymerisable monomers include a comonomer of the general formula VI



35      where  $Y'$  is an ethylenically unsaturated polymerisable group selected from



and



5

where R<sup>14</sup> is selected from the group consisting of hydrogen and C<sub>1</sub>-C<sub>4</sub> alkyl,

A' is -O- or -NR<sup>15</sup>- where R<sup>15</sup> is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl groups and groups

10

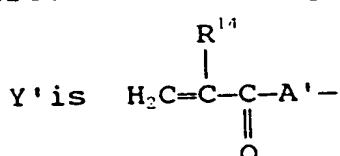
<sup>15</sup> K<sup>1</sup> is selected from the group consisting of -(CH<sub>2</sub>)<sub>1</sub>OC(O)-, -(CH<sub>2</sub>)<sub>1</sub>C(O)O-, -(CH<sub>2</sub>)<sub>1</sub>OC(O)O-, -(CH<sub>2</sub>)<sub>1</sub>NR<sup>16</sup>-, -(CH<sub>2</sub>)<sub>1</sub>NR<sup>16</sup>C(O)-, -(CH<sub>2</sub>)<sub>1</sub>C(O)NR<sup>16</sup>-, -(CH<sub>2</sub>)<sub>1</sub>NR<sup>16</sup>C(O)-, -(CH<sub>2</sub>)<sub>1</sub>OC(O)NR<sup>16</sup>-, -(CH<sub>2</sub>)<sub>1</sub>NR<sup>16</sup>C(O)NR<sup>16</sup>- in which the groups R<sup>16</sup> are the same or different), -(CH<sub>2</sub>)<sub>1</sub>O-, -(CH<sub>2</sub>)<sub>1</sub>SO<sub>3</sub>- and a bond, in which l is from 1 to 12 and R<sup>16</sup> is selected from the group consisting of hydrogen and C<sub>1</sub>-C<sub>4</sub> alkyl groups; and

Q is selected from the group consisting of straight and branched alkyl, alkoxyalkyl and (oligo-alkoxy)alkyl groups containing 6 to 24 carbon atoms, any of which groups is unsubstituted or substituted by one or more fluorine atoms and optionally contains one or more carbon-carbon double or triple bonds; and

siloxane groups  $-(CR^{16a})_{qq}(SiR^{16b})_{pp}R^{16b}$  in  
 which each group  $R^{16a}$  is the same or different and is  
 selected from the group consisting of hydrogen, alkyl  
 groups of 1 to 4 carbon atoms and aralkyl groups, each  
 group  $R^{16b}$  is alkyl of 1 to 4 carbon atoms,  $qq$  is from 1 to  
 6 and  $pp$  is from 0 to 49.

6 a process according to claim 5 in which

35



in which R<sup>11</sup> is methyl and A' is -O- and Q is an alkyl group of the formula -(CR<sup>17</sup>)<sub>n</sub>CR<sup>17</sup>, wherein the groups -(CR<sup>17</sup>)<sub>n</sub>- are the same or different and in each group -(CR<sup>17</sup>)<sub>n</sub>- the groups R<sup>17</sup> are the same or different and each group R<sup>17</sup> is selected

from the group consisting of hydrogen, C<sub>1-4</sub>-alkyl and -fluoroalkyl and fluorine and m is in the range 5 to 23.

5. A process according to claim 6 in which the said comonomer is selected from the group consisting of n-dodecyl methacrylate, octadecyl methacrylate, hexadecyl methacrylate, 1H,1H,2H,2H-heptadecafluorodecyl methacrylate, p-octyl styrene, p-dodecyl styrene and monomethacryloxypropyl terminated siloxanes.

8. A process according to claim 7 in which the said 10 comonomer is dodecyl methacrylate.

9. A process according to claim 1 in which the said radical polymerisable monomers include a diluent monomer selected from the group consisting of C<sub>1-4</sub>-alkyl(alk)acrylates, N,N-dialkylamino alkyl(alk)acrylates 15 containing 1 to 4 carbon atoms in each N-alkyl group and 1 to 4 carbon atoms in the alkylene group, C<sub>1-4</sub>-alkyl(alk)acrylamide, hydroxy C<sub>1-4</sub>-alkyl(alk)acrylate, N-vinyl lactam having 5-7 atoms in the lactam ring, styrene, derivatives of styrene having ring substituents 20 selected from C<sub>1-4</sub>-alkyl groups and halogen atoms, polyhydroxyl (alk)acrylates, alkenes, butadiene, maleic anhydride and acrylonitrile.

10. A process according to claim 9 in which the diluent monomer is selected from hydroxy C<sub>1-4</sub>-alkyl(alk)acrylates 25 and polyhydroxyl(alk)acrylates.

11. A process according to claim 1 in which the said radical polymerisable monomers include at least 5% by weight zwitterionic monomer and at least 0.1% by weight monomer having a reactive group.

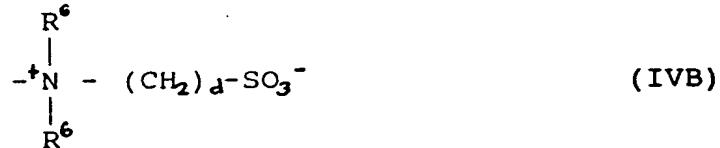
30 12. A process according to claim 9 in which the said radical polymerisable monomers include at least 5% by weight zwitterionic monomer, at least 0.1% by weight monomer having a reactive group and 5 to 20% by weight diluent monomer.

35 13. A process according to claim 5 in which the said radical polymerisable monomers include at least 5% by weight zwitterionic monomer, at least 0.1% by weight

monomer having a reactive group and 5 to 90% by weight of said comonomer.

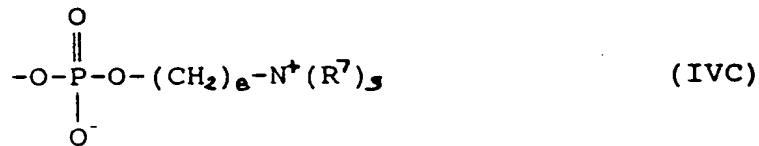
14. A biocompatibilising process in which a substrate having a surface which bears substrate pendant functional groups is biocompatibilised by coating it with a coating composition containing a polymer formed from a radical polymerisable monomers including a radical polymerisable zwitterionic monomer and a radical polymerisable monomer containing a reactive group to form a polymer having zwitterionic groups and pendant reactive groups and the said pendant reactive groups are reacted to form covalent bonds with said substrate pendant functional group and thereby form a stable coating of polymer on the said surface.

15. 15. A process according to claim 14 in which the zwitterionic group is a group X selected from groups IVB, IVC, IVD, IVE and IVF in which group IVB has the formula



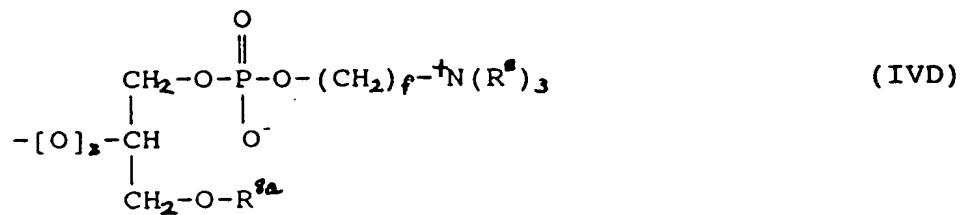
wherein the groups  $R^6$  are the same or different and each is hydrogen or  $C_{1-4}$  alkyl and d is from 2 to 4;

group IVC has the formula



where the groups  $R^7$  are the same or different and each is hydrogen or  $C_{1-4}$  alkyl, and e is from 1 to 4;

group IVD has the formula

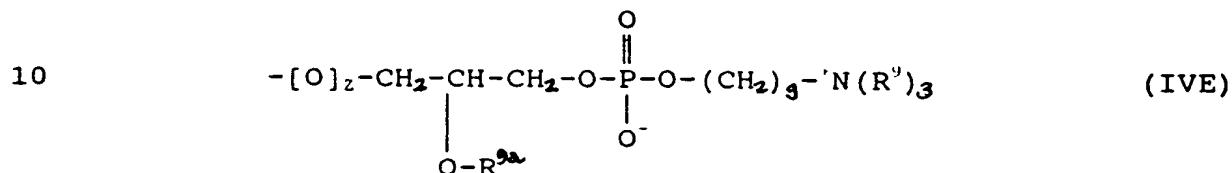


wherein the groups  $R^8$  are the same or different and each is hydrogen or  $C_{1-4}$  alkyl,  $R^{8a}$  is hydrogen or a group  $-C(O)B^1R^{8b}$

wherein R<sup>91</sup> is hydrogen or methyl, B<sup>1</sup> is a valence bond or straight or branched alkylene, oxaalkylene or oligo-oxaalkylene group, and f is from 1 to 4; and if B is other than a valence bond z is 1 and if B is a valence bond z is 0, if X is directly bonded to an oxygen or nitrogen atom and otherwise z is 1;

5      0, if X is directly bonded to an oxygen or nitrogen atom and otherwise z is 1;

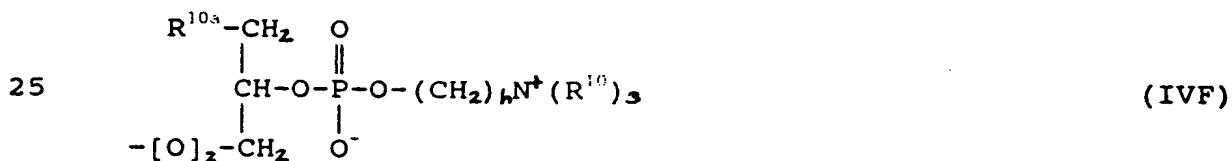
group IVE has the formula



wherein the groups R<sup>9</sup> are the same or different and each is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, R<sup>92</sup> is hydrogen or a group -C(O)B<sup>2</sup>R<sup>93</sup>, wherein R<sup>93</sup> is hydrogen or methyl, B<sup>2</sup> is a valence bond or a straight or branched alkylene, oxaalkylene or oligo-oxaalkylene group, and g is from 1 to 4; and

15      if B is other than a valence bond z is 1 and if B is a valence bond z is 0 if X is directly bonded to an oxygen or nitrogen atom and otherwise z is 1; and

group IVF has the formula

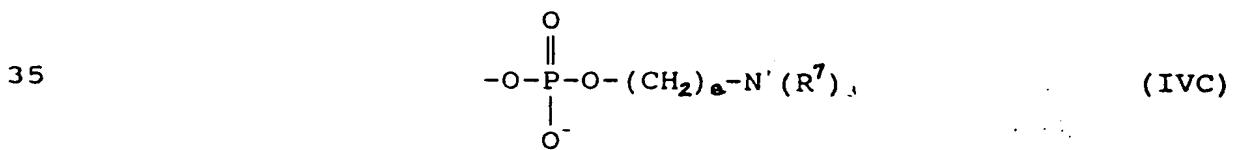


wherein the groups R<sup>10</sup> are the same or different and each is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, R<sup>10a</sup> is hydrogen or a group -C(O)B<sup>3</sup>R<sup>10b</sup> wherein R<sup>10b</sup> is hydrogen or methyl, B<sup>3</sup> is a valence bond or a straight or branched alkylene, oxaalkylene or oligo-oxaalkylene group, and h is from 1 to 4; and

25      if B is other than a valence bond z is 1 and if B is a valence bond z is 0 if X is directly bonded to the oxygen or nitrogen and otherwise z is 1.

16. A process according to claim 14 in which the pendant functional group on the polymer is a group Q<sup>3</sup> selected from the group consisting of aldehyde groups; silane and siloxane groups containing one or more substituents 40 selected from halogen atoms and C<sub>1</sub>-C<sub>4</sub>-alkoxy groups;

- hydroxyl; amino; carboxyl; epoxy;  $-\text{CHOHCH}_2\text{Hal}$  (in which Hal is selected from chlorine, bromine and iodine atoms); succinimido; tosylate; triflate; imidazole carbonyl amino; optionally substituted triazine groups; aceloxy; mesylate;
- 5      carbonyl di(cyclo)alkyl carbodiimidoyl; and oximino.
17. A process according to claim 15 in which the pendant functional group on the polymer is a group Q' selected from the group consisting of aldehyde groups; silane and siloxane groups containing one or more substituents
- 10     selected from halogen atoms and  $\text{C}_{1-4}$ -alkoxy groups; hydroxyl; amino; carboxyl; epoxy;  $-\text{CHOHCH}_2\text{Hal}$  (in which Hal is selected from chlorine, bromine and iodine atoms); succinimido; tosylate; triflate; imidazole carbonyl amino; optionally substituted triazine groups; aceloxy; mesylate;
- 15     carbonyl di(cyclo)alkyl carbodiimidoyl; and oximino.
18. A process according to claim 16 in which the pendant functional group is selected from the group consisting of aldehyde, reactive silane and siloxane amino, epoxy,  $\text{CHOHCH}_2\text{Hal}$  (in which Hal is halogen), succimimido,
- 20     tosylate, triflate, imidazolecarbonyl amino and optionally substituted triazine groups.
19. A process according to claim 17 in which the pendant functional group is selected from the group consisting of aldehyde, reactive silane and siloxane amino, epoxy,
- 25      $\text{CHOHCH}_2\text{Hal}$  (in which Hal is halogen), succimimido, tosylate, triflate, imidazolecarbonyl amino and optionally substituted triazine groups.
20. A process according to claim 14 in which the surface pendant groups are selected from the group consisting of
- 30     hydroxyl, carboxyl and amine groups.
21. A process according to claim 14 in which the zwitterionic group is a group of formula IVC



where the groups  $\text{R}^7$  are the same or different and each is hydrogen or  $\text{C}_{1-4}$  alkyl, and e is from 1 to 4;

the pendant functional group of the polymer is an  
amine group and

the pendant functional group on the substrate surface  
is a carboxyl group and in which the said covalent bond  
5 which is formed is an amide bond.